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THE PREPARATION AND CHARACTERIZATION OF MIXTURES OF POLYCYCLOPE--ETC(U)

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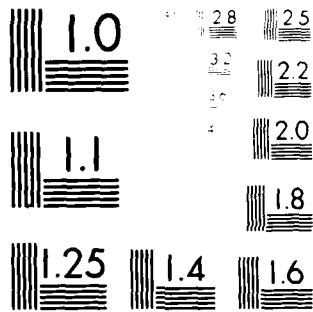
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
-Conditions for the thermal polymerization of cyclopentadiene to tetracyclopentadienes and higher molecular weight oligomers are given for both neat and solution polymerization modes. Density and volumetric heats of combustion are given for the mixtures of oligomers formed under different conditions. Compatibilities of oligomers with hydroxyl terminated polybutadiene (HTPB) are given.		

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AS SOLID RAMJET FUELS - FINAL REPORT

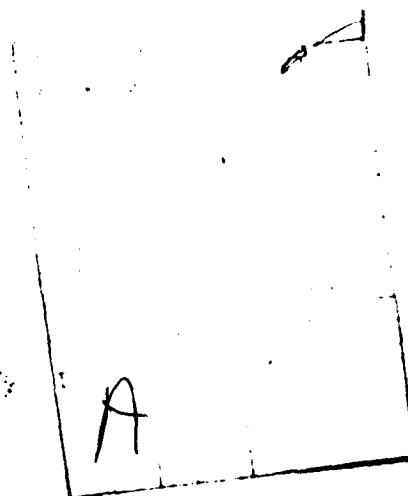
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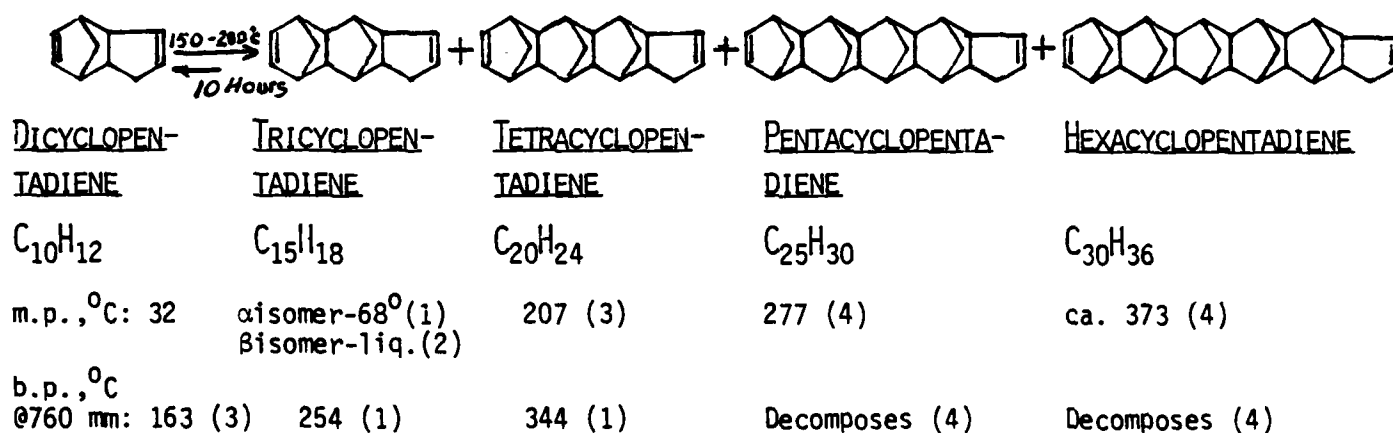
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SECTION I

INTRODUCTION

The objective of this work was to prepare and characterize a number of cyclopentadiene oligomers as possible candidate solid ramjet fuels. Commercial cyclopentadiene is available in high purity as a dimer, dicyclopentadiene. Upon heating at 150°C and higher under autogenous pressure in a closed system, this compound readily forms tricyclopentadiene and higher cyclopentadiene oligomers.



The lower boiling di and tricyclopentadienes are not suitable for solid ramjet fuels because they are low melting and create a condition called "balling" when mixed with HTPB binder.⁽⁵⁾ The tetracyclopentadienes and higher oligomers are high melting and do not contribute to this problem. They are amorphous solids which can be pulverized readily when free of dimer and trimer contamination. The latter can be removed by vacuum distillation or extraction with a low boiling hydrocarbon such as pentane or hexane followed by heating the oligomer mixture under vacuum to remove the solvent.

To be considered as suitable for solid ramjet fuels, these oligomers must also possess high volumetric heats of combustion and high densities in conjunction with good compatability with hydroxyl-terminated polybutadiene binder. Polycyclopentadiene oligomers larger than the trimer satisfy these conditions. Such mixtures have densities ranging from 1.03 to 1.15 and net volumetric heats of combustion as high as 172,000 BTU/gal.

In order to achieve acceptable reaction rates and high yields of cyclopentadiene oligomers within reasonable reaction times, temperatures greater than 170°C are required. However, the desirable products are extremely high melting and are vulnerable to thermal cracking, degradation and cross linking.⁽⁴⁾ Adequate agitation and good heat transfer become difficult under these circumstances particularly when a neat polymerization operation is employed. Consequently solution polymerization was adopted to overcome these difficulties, Toluene ⁽⁷⁾ was chosen as the solvent medium for these reactions because it provided an effective solvent for the di and tricyclopentadiene and an antisolvent for the higher oligomers thus controlling excessive cross linking to some degree.

The oligomers reported herein were made by both neat and solution polymerization modes and the experimental conditions, yields of oligomers higher than tricyclopentadiene and essential properties of the candidate solid ramjet fuels, i.e. net volumetric heat of combustion, density and compatability with HTPB are given in Table IV.

SECTION II

SUMMARY & CONCLUSIONS

Dicyclopentadiene was thermally polymerized both neat and in solution with toluene. The temperature ranges investigated were between 180°C and 298°C in solution and 200°C to 265°C in neat polymerizations. The highest net volumetric heat of combustion, 172,000 BTU/gallon, the highest density and good compatibility with HTPB binder were obtained in neat polymerizations at 200°C and 240°C. The neat thermal polymerizations had a serious drawback, i.e. difficulty in controlling reaction temperatures. High reaction temperatures can result in crosslinking which can account for the lower densities of the oligomers and lower net volumetric heats of combustion as indicated in the neat experiment at 265°C and the solution experiments @ 281 and 298°C. These oligomers were dark colored and showed high C/H ratios.

Solution polymerization of cyclopentadiene gave excellent yields (90-95%) of tetramers and higher oligomer mixtures at 281°C and 298°C but the volumetric heats of combustion were lower than those of the neat polymerization products. At these temperatures, the net volumetric heats of combustion, i.e., 154,872 and 152,395 BTU/gallon and their densities were the lowest obtained in both types of polymerization. These oligomers were darker in color and only slightly soluble in boiling toluene. Such properties, i.e. insolubility in boiling toluene, low density and dark color indicate crosslinking, a result of excessively high reaction temperatures and reaction times. With the exception of the product from the 231°C run, the oligomers

formed by solution polymerization were very compatible with HTPB binder. The poor behavior of the 231°C product in this respect is probably due to contamination by lower molecular weight material which was not completely removed by the distillation.

Despite these adverse properties, the use of solution polymerization of cyclopentadiene to make acceptable solid ramjet fuels should be investigated further, especially in a continuous system,. With good temperature control, high temperatures and shorter reaction times are more attainable than in a batch process; and consequently higher yields of tetramer and larger oligomer mixtures might be realized without crosslinking.

SECTION III

PREPARATION OF CANDIDATE SOLID RAMJET FUELS

A. Objectives

1. To prepare mixtures of polycyclopentadiene oligomers which have the following properties:
 - a. High net volumetric heat of combustion.
 - b. High density.
 - c. Compatible formulation with hydroxyl-terminated polybutadiene binder (HTPB)
2. Define the operating conditions for preparing these oligomers.
3. Prepare samples of these oligomers for evaluation at the Naval Weapons Center at China Lake.

B. Procedure:

Cyclopentadiene dimer (Table I - Elemental Analysis and Properties) was thermally polymerized in a closed, magnetically stirred autoclave, one gallon capacity and/or a stainless steel Parr reactor (2 liter capacity) at temperatures of 200°C and higher for such reaction times as were required to minimize tricyclopentadiene content of the product and maximize the yields of tetracyclopentadiene and higher oligomers. The reactors were heated externally by an electric furnace and were equipped with internal and external thermocouples to monitor the reaction and skin temperatures.

Both neat and solution polymerizations were studied. Neat polymerizations were done in the Parr reactor. Internal agitation was not employed here because the gelatinous and solid oligomers cavitated at the impeller site.

The solution polymerizations were carried out in a one gallon magnetically stirred and electrically heated autoclave. Temperature control was governed by the reaction temperature.

The polymerization reactions were monitored by gas chromatography of the total product (ASTM method D-2887), using a C_{17} paraffin as an internal standard. Oligomers up to and including hexacyclopentadienes were resolved sufficiently by this technique to identify the isomer groups. Higher boiling oligomers were reported as >hexacyclopentadiene components. A Hewlett Packard 7620-A instrument equipped with an 18" long 1/16" diameter s.s. OV-1 column and a flame ionization detector was employed for this purpose. Helium flow rate = 34 cc/min. with a temperature programmed for 15°/min. over a range of 70-380°C.

Distillations of the final reaction product were made at one atmosphere to 150°C overhead temperature and 190°C pot temperature to remove light ends and at 0.4 mmHg pressure and pot temperature of 200°C to remove residual dimer and tricyclopentadienes.

Gross heats of combustion were determined by bomb calorimeter using the ASTM D240 method. Net heats of combustion were calculated from gross heats of combustion using the formulae:

$$H_n = 1.8 H_g - 91.23 \times H$$

or

$$H_n = 4310 + (0.7195)(1.8)(H_g)$$

where H_n = net heat of combustion, BTU/lb.
 H_g = gross heat of combustion, cal/g
 H = Hydrogen content of sample, %

Densities of the candidate ramjet fuels were measured at the China Lake Naval Weapons Center through the courtesy of Mr. G. W. Burdette.

C. Neat Polymerization

A two liter stainless steel Parr reactor was used to prepare polycyclic oligomers from neat dicyclopentadiene. One thousand grams of dicyclopentadiene were used in each experiment and the reaction temperatures investigated were 200°C, 240°C and 260°C.

At 200°C and 72.5 hours reaction (soaking) time thirty weight percent of the products is recycle material i.e. di and tricyclopentadienes. The residue has a density of 1.15 and a net volumetric heat of combustion of 172,191 BTU/gallon and was compatible with HTPB binder.

At 240°C and a reaction time of 2.83 hours cyclopentadiene dimer gave a heterogenous product which, when cooled to room temperature consisted of two solid phases, In this experiment the product was cooled slowly over a period of 16 hours in contrast to the other experiments where rapid quenching was used to stop the reaction. The two phases were easily separated mechanically and contained very different distributions of components. The more dense phase ($d_{20/4} = 1.15$) did not require a distillation to remove the light ends which did not exceed 5% (area) and consisted primarily of a tricyclopentadiene. The net volumetric heat of combustion of this dense phase was 172,000 BTU/gallon. This material burned very rapidly in oxygen with such explosive force that it was difficult to measure its heat of combustion.

The less dense phase required a distillation to remove the trimers. The residue from this distillation had a 6% lower net volumetric heat of combustion, i.e. 161,291 BTU/gallon than the more dense phase and its density was lower ($d_{20/4} = 1.09$). The overall yield of this lighter material was 52.9%. The yield of combined residues from this experiment = 85.4 wt.%.

The polymerization @ 265°C for 4.6 hours gave a high density product ($d_{20/4} = 1.10$) which did not require a removal of light ends. Surprisingly, this material had a lower net volumetric heat of combustion (158,254 BTU/gallon). This oligomer was dark brown to black in color and only slightly soluble in boiling toluene and was probably crosslinked. It had not been formulated with HTPB. Residues from the polymerizations at 200°C and 240°C had been cast successfully with HTPB binder and were light yellow to caramel in color.

These data in addition to the experimental conditions are given in Table II.

D. Solution Polymerization of Cyclopentadiene

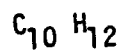
Solution polymerizations of cyclopentadiene dimer in toluene solvent were performed in a one gallon magnetically stirred and electrically heated autoclave. The weight ratio of dimer to toluene was 1:1. Temperature control was governed by the reaction temperature. These polymerization studies were made over a temperature range of 180°C to 298°C.

Tricyclopentadiene was the major product of the polymerizations conducted between 180°C and 281°C. At 231°C, tetracyclopentadienes and higher oligomers were formed in significant amounts. At 281° and 298°C better than 90

wt.% of the products were of a higher molecular weight than hexamers. These high molecular weight oligomers had densities varying from 1.1 to 1.03, with the lower density oligomers having been formed at the higher reaction temperatures, i.e. 281°C and 298°C.

The net volumetric heats of combustion of the high molecular weight oligomers also decreased with increasing reaction temperatures. With the exception of the experiment @ 231°C, the high molecular wt. oligomers formed in the solution polymerization experiments were formulated satisfactorily with HTPB binder. The polymers prepared @ 281° and 298°C were amber colored in contrast to the light green and cream colored oligomers formed at 180-231°C and showed only slightly solubility in boiling toluene. These properties and C/H ratios of 0.86 and higher suggest that crosslinking had occurred at the high temperature. These data are summarized in Table III.

TABLE I
CYCLOPENTADIENE DIMER



C	90.36 wt.%
H	9.05 "
O	0.62 "
N	0.03 "
Density 20/4	0.9891
Spec. grav. 60/60°F	0.9928
Boiling point, °C	163
Melting Point, °C	32

TABLE II
POLYMERIZATION OF NEAT DICYCLOPENTADIENE

<u>EXPERIMENT NO.</u>	<u>743144</u>	<u>743150-6</u>	<u>743142-3P</u>	<u>743140</u>
<u>Reaction Temp. °C</u>	<u>200</u>	<u>240</u>		<u>265</u>
Charge (Dicyclopentadiene) (g)	1000	1000		1000
Preheat Time, Hrs.	1.5	1.75		1.9
Reaction Time, Hrs.	72.5	2.83		4.6
Max. Pressure, psig	52	50		68
Total Product Analysis		<u>67.5%(1)</u>	<u>32.5%(1)</u>	
Dicyclopentadienes	4.4	(45.13)	(4.93)	(2.84)
Tricyclopentadienes	32.1			
Tetracyclopentadienes	24.6	19.75	4.17	1.62
Pentacyclopentadienes	20.6	17.48	3.68	0.44
Hexacyclopentadienes	11.64	9.19	3.02	1.05
>Hexacyclopentadienes	6.6	8.45	84.20	94.05
<u>Distillation</u>				
Pot Temp., °C	235	170	Not	Not
Pressure mm Hg	0.36	0.38	distilled	distilled
<u>Yield, Wt.%</u>				
<Tetracyclopentadienes	29.3	19.3		
Residue, Tetracyclopentadienes +	70.7	80.7		
<u>Properties of Residue</u>				
d 20/4	1.15	1.09	1.15	1.10
Gross BTU/lb	18,780	18,571	18,780	18,076
Net BTU/lb	17,975	17,749	17,975	17,271
Net BTU/gal	172,191	161,291	172,200	158,254
C, wt.%	90.88	90.99	90.81	91.08
H, wt.%	9.12	9.01	9.19	8.91
C/H	0.830	0.842	0.823	0.852
Color	Lt. Yellow	Butter-scotch	Caramel	Brown-black

(1) Two solid phases separated on slow cooling over 16 hour period.

TABLE III

SOLUTION POLYMERIZATION OF DICYCLOPENTADIENE

<u>Experiment No.</u>	<u>743145</u>	<u>743152</u>	<u>743154</u>	<u>743156</u>	<u>743167</u>	<u>743180-2</u>
Dicyclopentadiene/Toluene (wt)	1	1	1	1	1	1
Preheat Time, Hrs	1.33	3.3	2.75	2.65		
Reaction Temp., °C	180	185	201	231	281	298
Reaction Time, Hrs.	4.75	1.8	3.3	3.65	3.50	3.25
Max. Pressure, psig	72	68	42	125	317	425
<u>Product Analysis, area %</u>						
Dicyclopentadienes	57.13	48.17	40.57	10.22	0.99	4.77
Tricyclopentadienes	37.54	46.00	42.08	48.40	0.90	Trace
Tetracyclopentadienes	4.83	5.62	14.65	25.83	1.07	3.18
Pentacyclopentadienes	0.50	0.19	2.65	10.52	0.83	3.10
Hexacyclopentadienes	Trace	Trace	0.06	5.02	0.79	2.63
>Hexacyclopentadienes	0	Trace	Trace	Trace	95.41	86.37
<u>Distillation</u>						
Overhead Temp., °C	140	Not	Not	182	171	(1)
Pot Temp., °C	178	Distilled	Distilled	225	178	202
Pressure mm Hg	0.14			0.3	0.2	0.3
<u>Yield, Wt. %</u>						
<Tetracyclopentadienes	94.8			57.99	8.5	4.53
Residue, Tetracyclopentadienes +	5.2			42.01	91.5	95.47
<u>Properties of Residue</u>						
d 20/4	1.10			1.09	1.04	1.03
Gross BTU/lb	18,722			18,945	18,642	18,554
Net BTU/lb	17,921			18,105	17,862	17,774
Net BTU/gal	164,348			164,526	154,872	152,395
C, wt. %	91.22			90.68	91.45	91.15
H, wt. %	8.78			9.32	8.55	8.85
C/H	0.866			0.811	0.891	0.858
Color	Cream			Green, white & sticky	Amber	Dark Amber

1 Insufficient light ends to get OVHD T

TABLE IV

PROPERTIES OF CANDIDATE POLYCYCLOPENTADIENE SOLID RAMJET FUELS

Polymerization Type	SOLUTION POLYMERIZATION				NEAT POLYMERIZATION			
Reaction Time, Hrs.	4.75	3.65	3.50	3.25	72.5	(3) 2.83		4.6
Reaction Temp., °C	180	231	281	298	200	240		265
Density, 20/4	1.10	1.09	1.04	1.03	1.15	1.09	1.15	1.10
Net BTU/Gal	164,348	164,526	154,872	152,395	172,191	161,291	172,200	158,254
Yield, Wt.%	5.2	42.01	91.50	95.47	70.7	54.5	32.5	100
HTPB, Compatability	?(2)	NG(1)	Good	Good	?(2)	Good	Good	?(2)

(1) Product is sticky and still contains some trimer.

(2) Not formulated yet. Solids are dry and easily ground.

(3) Product of Polymerization contains 2 solid phases. Each phase was evaluated separately.

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